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ON THE PRESSURE BROADENING OF THE MOLECULAR SPECTRA

I. THE LIOUVILLE SPACE METHODS

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The general expression for the line shapes of the molecular absorption, emission and Raman spectra broadened by the collision is analyzed in terms of the Liouville space methods. Some general relations following from the Liouville space symmetries are presented. The effect of the radiating molecule translational motion and the collision induced velocity change is taken into account. The structure of particular branches is discussed.

1. *Introduction*

It is generally recognized that the Liouville space formalism describes the relaxation phenomena in the simplest way. It has appeared, although somewhat hidden, in the pressure broadening theory in a paper by Anderson [1]. Some years later the Liouville space method had been used by Baranger [2] in the theory of atomic line broadening, and by Fiutak and Van Kranendonk [3] in the Raman line broadening problem. The essential progress is due to Fano [4], who has adopted the projection operator method of Zwanzig [5] to the line shape problem.

In the present paper we intend to work out these relations, which are generally satisfied in the binary collision approximation. On the other hand, we will consider some approximations, which as we hope, may enlighten us to the physical significance of the relaxation operator. In the next section we will shortly present the main results of the projection operator method based on the concept of the Liouville space method as the Hilbert space of the so-called Hilbert–Schmidt operators with the trace metric. This was already done, in connection with the line shape problem, by one of authors [6] on the basis of the Fano theory.

In this section we will recall also the symmetries in the Liouville space and in that we will follow the paper of Ben-Reuven [7] and the paper [6] complementary to it. In the

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third section the general formula for the relaxation operator will be specified in order to single out the influence of the velocity changing collisions and the rotational transitions on the line shape. In particular there is a rather non trivial coupling between the Doppler and pressure broadening well known in the atomic spectroscopy and laser physics (see e.g. [8–10]). This effect is also present in the molecular spectra and, as we shall see, its description is much the same as in the atomic spectroscopy.

2. *The Liouville space in the pressure broadening theory*

The usefulness of the Liouville space methods in the line shape and related problems results from the fact that the line contour is generally given as the Fourier transform of the following autocorrelation function

$$U(t) = \mathrm{Tr}\,(\varrho X^{(s)} e^{\frac{i}{\hbar}Ht} X^{(s)} e^{-\frac{i}{\hbar}Ht}) \qquad (1)$$

of an operator $X^{(s)}$ which represents the radiating molecule in its interaction with the electromagnetic field. We will use the so-called trace metric in the Liouville space method which is defined by the following scalar product

$$(A, B) = \mathrm{Tr}\,(A^{\dagger}B) \qquad (2$$

for two operators, A and B, which are assumed to be Hilbert–Schmidt operators, i.e. the norms $\mathrm{Tr}(A^{\dagger}A)$ and $\mathrm{Tr}(B^{\dagger}B)$ are finite. With that definition of the scalar product, the autocorrelation function (1) becomes

$$U(t) = (X^{(s)}\sqrt{\varrho}\,,\ e^{\frac{i}{\hbar}\hat{H}t} X^{(s)}\sqrt{\varrho}) \qquad (3)$$

provided that the square root $\sqrt{\varrho}$ of the density matrix commutes with the Hamiltonian H of the system, which is usually so with at least sufficient accuracy. The square root of the density matrix is not uniquely defined by the relation

$$(\sqrt{\varrho})^2 = \varrho, \qquad (4)$$

so we may require it to be a positively defined operator. The Liouville space Hamiltonian $\hat{H}$ is defined as follows

$$\hat{H}A = AH - HA. \qquad (5)$$

Usually, in the irreversibility theory, the Liouvillians are defined with the opposite sign. The change of the notation reflects the fact that we are looking for the time evolution of the operator in the Heisenberg picture rather than the dynamics of the density matrix.

The main problem in the theory of relaxation processes, and in particular the theory of the collisional broadening, is the elimination of the thermal bath either directly from (3) or after we pass to the frequency distribution function $I(\omega)$, which is given as the Fourier transform

$$I(\omega) = \frac{1}{\pi} \lim_{\mathrm{Im}\,\omega \to 0^{+}} \mathrm{Im} \left(X^{(s)}\sqrt{\varrho}\,,\ \frac{1}{\hat{H}-\omega} X^{(s)}\sqrt{\varrho} \right) \qquad (6)$$

of the $X^{(s)}$ — autocorrelation function. To this end we assume, for the sake of simplicity, that the square root of the density matrix of the whole gas factors in the following way:

$$\sqrt{\varrho} = \sqrt{\varrho^b}\sqrt{\varrho^s}, \tag{7}$$

i.e. into the product of the square roots of the thermal bath density matrix ϱ^b and the density matrix of the radiating system ϱ^s. The bath will be eliminated by means of the projection operator $\hat{P}^b_\varrho$ defined as follows:

$$\hat{P}^b_\varrho A = \sqrt{\varrho^b}\,\mathrm{Tr}\,(\sqrt{\varrho^b}\,A), \tag{8}$$

where the trace is over the states of the bath. As usual, we may look after the time relaxation of the system according to the following equation:

$$ih\frac{\partial\langle X^{(s)}\rangle_b}{\partial t} = \hat{H}_s\langle X^{(s)}\rangle_b$$

$$-\frac{i}{h}\int\limits_0^t dt'\,\mathrm{Tr}\,(\sqrt{\varrho^b}\,\hat{H}_{sb}(1-\hat{P}^b_\varrho)e^{-\frac{i}{h}\hat{H}'(t-t')}(1-\hat{P}^b_\varrho)\hat{H}_{sb}\sqrt{\varrho^b})\,\langle X^{(s)}\rangle_b, \tag{9}$$

where $\langle X^{(s)}\rangle_b$ stands for the $X^{(s)}$ operator averaged over bath at time t, i.e.

$$\langle X^{(s)}(t)\rangle_b = \mathrm{Tr}\,(\sqrt{\varrho^b}\,e^{\frac{i}{h}\hat{H}t}X^{(s)}\sqrt{\varrho^b}). \tag{10}$$

The other way is to start from the expression (6) for the intensity distribution obtaining

$$\mathrm{Tr}\left(\sqrt{\varrho^b}\,\frac{1}{\hat{H}-\omega}\sqrt{\varrho^b}\,X^{(s)}\right) = \frac{1}{\hat{H}_s+\hat{\Phi}(\omega)-\omega}X^{(s)}, \tag{11}$$

with the relaxation operator $\hat{\Phi}(\omega)$ given by

$$\hat{\Phi}(\omega)A^{(s)} = \lim_{\mathrm{Im}\,\omega\to 0+}\mathrm{Tr}\left(\sqrt{\varrho^b}\,\hat{H}_{sb}(1-\hat{P}^b_\varrho)\frac{1}{\hat{H}'-\omega}(1-\hat{P}^b_\varrho)\hat{H}_{sb}\sqrt{\varrho^b}\,A^{(s)}\right). \tag{12}$$

In these relations H denotes the "diagonal" part of the Hamiltonian, i.e.

$$\hat{H}' = \hat{H}_s+\hat{H}_b+(1-\hat{P}^b_\varrho)\hat{H}_{sb}(1-\hat{P}^b_\varrho), \tag{13}$$

where the free system Hamiltonian H_s includes the bath averaged interaction Hamiltonian H_{sb} of the bath b and the system s.

An important feature of our relaxation operator $\hat{\Phi}(\omega)$ is the positive definiteness of its imaginary part, i.e.

$$\begin{aligned}\mathrm{Im}\,(A^{(s)}, \hat{\Phi}(\omega)A^{(s)}) &\geqslant 0 \quad \text{for} \quad \mathrm{Im}\,\omega > 0\\ &\leqslant 0 \quad \text{for} \quad \mathrm{Im}\,\omega < 0\end{aligned} \tag{14}$$

as it follows immediately from (12) and the definition of $\hat{P}^b_\varrho$ as the projection operator in the Hilbert space.

Formula (6) for the intensity distribution function combined with (11) leads to the following expression:

$$I(\omega) = \frac{1}{\pi} \operatorname{Im}\left(X^{(s)}\sqrt{\varrho^s}, \frac{1}{\hat{H}_s+\hat{\Phi}(\omega)-\omega} X^{(s)}\sqrt{\varrho^s}\right), \tag{15}$$

which reduces the line shape problem to the calculation of the relaxation operator $\hat{\Phi}(\omega)$. In the binary collision approximation (Fano [4]) this operator is given by

$$\hat{\Phi}(\omega)A^{(s)} = -N \lim_{\operatorname{Im}\omega\to 0^+} \operatorname{Tr}\left(\sqrt{\varrho^b}\,\hat{V}\frac{1}{\hat{H}_0+\hat{V}-\omega}\hat{V}\sqrt{\varrho^b}\,A^{(s)}\right), \tag{16}$$

where $\hat{H}_0$ stands for the combined free particle Hamiltonians of the radiating molecule and one perturber, while by $\hat{V}$ we denote their coupling. In this approximation the relaxation operator is proportional to the density of the perturbers, that is to the ratio of their total number N to the volume Ω.

For an isotropic medium the relaxation operator $\hat{\Phi}(\omega)$ is invariant with respect to the rotations generated by the Liouville space angular momentum operator $\hat{J}$ (see Ben-Reuven [7]) which is defined by

$$\hat{J}A = JA-AJ. \tag{17}$$

The irreducible tensors in ordinary space form a basis of the eigenvectors of $\hat{J}$. So the operator $X^{(s)}$ in (15) may be decomposed on the spherical tensors according to components X^{Π}_{JM}

$$X^{(s)} = \sum_{JM\Pi} X^{\Pi}_{JM}, \tag{18}$$

where J and M label the quantum numbers of $\hat{J}$, while Π stands for parity. Finally, each multipole component X^{Π}_{JM} contributes independently to the frequency distribution, function, i.e.

$$I(\omega) = \frac{1}{\pi} \operatorname{Im} \sum_{\Pi JM}\left(X^{\Pi}_{JM}, \frac{1}{\hat{H}_0+\hat{\Phi}^{\Pi}_{J}(\omega)-\omega} X^{\Pi}_{JM}\right). \tag{19}$$

The symmetry considerations have to be supplemented by the time reversal, which is effected by the anti-unitary operator $\hat{C}_+$ given by

$$\hat{C}_+A = A^\dagger. \tag{20}$$

Using the relations

$$(A, \hat{C}_+\hat{\Phi}(\omega)\hat{C}_+B) = (\hat{C}_+A, \hat{\Phi}(\omega)\hat{C}_+B)^*. \tag{21}$$

and

$$\hat{C}_+\hat{\Phi}(\omega)\hat{C}_+ = -\hat{\Phi}(-\omega^*), \tag{22}$$

we arrive at

$$(A^\dagger, \hat{\Phi}(-\omega^*)B^\dagger) = -(A, \hat{\Phi}(\omega)B)^*. \tag{23}$$

Particularly, for $A = B = X$ we get the following formula

$$(X^{\dagger}, \hat{\Phi}(-\omega^{*})X^{\dagger}) = -(X, \hat{\Phi}(\omega)X)^{*}, \tag{24}$$

which links the complex line shift of the transition generated by the operator X with the reverse generated by $X^{\dagger}$.

3. The line shapes of the vibrational-rotational transitions in the impact approximation

The line shape is given by a relatively simple formula in the impact approximation, under which the relaxation operator (16) does not depend on ω. The impact approximation consists of assuming the collision time to be much shorter than any other characteristic time which comes into question. Thus we may apply it to the frequency interval, in the vicinity of the line centre, which is small enough as compared against the inverse of the collision time. Practically, we may limit ourselves to this approximation as long as the pressure is not too high, so that the neighbouring lines do not overlap appreciably.

Our approach differs from the usual impact theory formulation in that it takes fully into account the velocity changes due to the collisions. To this end we introduce the Liouville space momentum eigenvectors $e_{\vec{p}_0\vec{\kappa}}$, which according to [10] are obtained by projecting the vectors $|\vec{p}_0\rangle\langle\vec{p}_0|$ on the subspace of given difference $\vec{\kappa}$ of the final state momentum $\vec{p}_0'$ and the initial one $\vec{p}_0$. Quite obviously, this difference is due to the recoil of the radiating molecule in effect of the radiation process. Furthermore, we have to use the Liouville space eigenvectors e_{if} of the radiating molecule internal energy, which we choose to be at the same time eigenvectors of the Liouville space angular momentum and parity with the corresponding eigenvalues J, M and Π, defined for the given radiation process according to (19). They are defined by the following relation

$$e_{if}(JM\Pi) = \sum_{m_i m_f} (-1)^{j_f - m_f}(2J+1)^{1/2} \begin{pmatrix} j_f & J & j_i \\ -m_f & M & m_i \end{pmatrix} |v_f j_f m_f\rangle\langle v_i j_i m_i| \tag{25}$$

in the Dirac notation with v, j and m standing for the vibrational, rotational and magnetic quantum numbers, respectively, for the initial state i or final f. With this notation, and after some rather straightforward calculations, which are essentially an extension of those previously done in [10], we get from (12) the following result:

$$\begin{aligned} &(e_{if}(JM\Pi)e_{\vec{p}'_0\vec{\kappa}}, \hat{\Phi}(\omega_{fi})e_{if}(JM\Pi)e_{\vec{p}_0\vec{\kappa}}) \\ &= n(2\pi)^3\langle\mathscr{T}_{ii}(\vec{p}\to\vec{p};\, m\to m) - \mathscr{T}^{*}_{ff}(\vec{p}\to\vec{p};\, m\to m)\rangle_{\mathrm{av}}\delta(\vec{p}_0-\vec{p}'_0) \\ &\quad + in(2\pi)^4(2J+1)\sum_{mm'}(-1)^{-m-m'}\begin{pmatrix} j_f & J & j_i \\ -m & 0 & m \end{pmatrix}\begin{pmatrix} j_f & J & j_i \\ -m' & 0 & m' \end{pmatrix} \\ &\quad \times\langle\mathscr{T}^{*}_{ff}(\vec{p}\to\vec{p}';\, m\to m')\delta(\varepsilon-\varepsilon')\mathscr{T}_{ii}(\vec{p}\to\vec{p}';\, m\to m')\rangle_{\mathrm{av}}, \end{aligned} \tag{26}$$

where the bracket $\langle\ldots\rangle_{\mathrm{av}}$ stands for the average over the perturber states of momentum and internal motion, by n we denote the density of the perturbers, while p and ε stand for the momentum and energy of the relative motion, respectively.

In the Doppler limit, that is for the density so low that a single collision suffices to produce a change of the Doppler shift larger than the collisional half-width, we may ignore the last term in (26). The spectrum is then composed of the particular vibrational rotational lines each of them represented by a corresponding line shape function given by

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Im}\int d_3\vec{p}_0\varrho(p_0)\,(\omega_{fi}-\omega+\hat{h}_0+n(2\pi)^3$$

$$\times\langle\mathcal{T}_{ii}(\vec{p}\to\vec{p};\,m\to m)-\mathcal{T}_{ff}(\vec{p}\to\vec{p};\,m\to m)\rangle_{\mathrm{av}})^{-1}. \tag{27}$$

A more refined approximation would consist of taking into acount the neglected last term of the relaxation operator (26) in much the same way as it has been done for atoms by Paul and one of the authors [11]. The collisional effects in formula (25) are overestimated for we assume that the radiation process is interrupted not only by the rotational transition but also by all velocity changing collisions. The intricacy of the formula (27), following from the velocity dependence of the amplitudes $\mathcal{T}_{ii}$ and $\mathcal{T}_{ff}$, forces us to test some further approximations. Therefore, it has been suggested in [11] that the $\mathcal{T}$-matrix has to be averaged over the p_0 components perpendicular to the z-axis, i.e. to the momentum transferred from the electromagnetic field to the molecule. If so, we end with a less complicated formula for the lineshape, namely

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Im}\int dp_{0z}\varrho(p_{0z})\left(\left(\omega_{fi}-\omega+\frac{\kappa p_{0z}}{m_0}+\frac{\kappa^2}{2m_0}\right)\right.$$

$$\left.+n(2\pi)^3\langle\mathcal{T}_{ii}(\vec{p}\to\vec{p};\,m\to m)-\mathcal{T}^{*}_{ff}(\vec{p}\to\vec{p};\,m\to m)\rangle_{\mathrm{av},\perp}\right)^{-1}, \tag{28}$$

where the bracket $\langle\ldots\rangle_{\mathrm{av},\perp}$ stands for the average over the perpendicular components of p_0 in addition to the bath averaging.

In this region of densities, where the collisional effects prevail over the Doppler broadening, we may ignore the recoil term and use the standard impact theory formula

$$I(\omega) = \frac{1}{\pi}\,\frac{w_{fi}}{(\omega_{fi}-\omega+d_{fi})^2+(w_{fi})^2}\,. \tag{29}$$

Here the shift d_{fi} and the half-width w_{fi} are obtained by averaging the whole relaxation operator (26) over the p_0 states distribution, including the z-component of it. In this case the broadening is mainly due to the rotational relaxation and reorientation of the radiating molecule in the course of collision. As it is clear from quoted papers [10, 11], the region of densities, where the pressure broadening competes with the Doppler one, may be, to some extent, included in our present considerations by taking into account the respective corrections of formula (28) or (29). On the other hand, these two formulas may not produce a good enough description of the line shape, even in this region of densities, where they are supposed to be valid, if the dependence of the bath averaged $\mathscr{T}$-matrix elements on the velocity of the radiating molecule is too pronounced. Even so, the corrections introduced according to the method proposed in [10] will improve the accuracy in a relatively easy way.

The line shape calculations are usually facilitated by ignoring the dependence of the scattering matrix on the vibrational state. This approximation leads to a symmetry of the line shape function of the corresponding transitions of the P and R, as well as O and S branches. In fact, the relation (23) implies that the normalized line shape function of the $j \to j+\Delta j$ transition shows a mirror symmetry with respect to that of the $j+\Delta j \to j$ transition, if we forget about the vibrational states. The whole difference between the intensities distribution in P and R or O and S branches comes from the population factor. However, the experimental evidence of this symmetry is not always clear. Another test for our guess, that the scattering process depends weakly on the vibrational state, is the narrowing of the Q-branch (compare [12]). In fact, if we disregard the vibrational-rotational coupling term in the energy and in the scattering matrix, the Q-branch is represented by a single line (see Appendix) with the relaxation operator $\Phi^{Q}(\omega_{fi}^{(0)})$ averaged over all transitions according to

$$\begin{aligned}\Phi^{Q}(\omega_{fi}^{(0)}) = in(2\pi)^3 \sum_{j} \varrho(E_j) \Bigg(&\mathrm{Im}\, \langle \mathscr{T}_{jj}(\vec{p} \to \vec{p}; m \to m) \rangle_{\mathrm{av}} \\ &\times \delta(\vec{p}_0 - \vec{p}_0') + 2\pi(2J+1) \sum_{j'mm'} (-1)^{j+j'-m-m'} \begin{pmatrix} j & J & j \\ -m & 0 & m \end{pmatrix} \begin{pmatrix} j' & J & j' \\ -m' & 0 & m' \end{pmatrix} \\ &\times \langle \mathscr{T}^{*}_{jj'}(\vec{p} \to \vec{p}\,'; m \to m') \delta(\varepsilon - \varepsilon') \mathscr{T}_{jj'}(\vec{p} \to \vec{p}\,'; m \to m') \rangle_{\mathrm{av}} \Bigg), \end{aligned} \tag{30}$$

where $\varrho(E_j)$ stands for the population factor of the rotational state j. For moderate densities, when the Doppler broadening may be neglected, this line has a lorentzian profile with the half-width given by

$$\begin{aligned}(\bar{e}(\vec{p}_0), \Phi^{Q}(\omega_{fi}^{(0)}) \bar{e}(\vec{p}_0)) = in(2\pi)^4 \sum_{jj'} \varrho(E_j) \int d_3\vec{p}_0 \varrho(\vec{p}_0) \int d_3\vec{p}_0\,' \\ \times \Bigg(\langle \mathscr{T}^{*}_{jj'}(p \to p'; m \to m) \delta(\varepsilon - \varepsilon') \mathscr{T}_{jj'}(\vec{p} \to \vec{p}\,'; m \to m) \rangle_{\mathrm{av}} + (2J+1) \sum_{mm'} (-1)^{j+j'-m-m'} \\ \times \begin{pmatrix} j & J & j \\ -m & 0 & m \end{pmatrix} \begin{pmatrix} j' & J & j' \\ -m' & 0 & m' \end{pmatrix} \langle \mathscr{T}^{*}_{jj'}(\vec{p} \to \vec{p}\,'; m \to m') \delta(\varepsilon - \varepsilon') \mathscr{T}_{jj'}(\vec{p} \to \vec{p}\,'; m \to m') \rangle_{\mathrm{av}} \Bigg)\end{aligned} \tag{31}$$

as it follows immediately from (30) after we average over the momentum states of the radiating molecule and use the optical theorem. Thus the broadening is entirely due to the reorientation effect of the collisions. Particularly, in the case of Raman scattering due to the isotropic part of the Raman tensor, i.e. for $J = 0$, there is no collisional broadening except some perturbation of the spectrum due to the velocity changing collisions.

APPENDIX

For the Q-branch neither the formula (26) nor the second one (27) are appropriate as a result of the strong overlap of the lines. In fact, for this branch all the transition frequencies are equal, provided that the vibration-rotation coupling term in the energy is small as this is usually the case. In accord with (19) the shape function is given by

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Im}\left(\bar{e}^{Q}_{if}(J0\Pi)\bar{e}(\vec{p}_0), \frac{1}{\omega^{(0)}_{fi}-\omega+\hat{h}_0+\hat{\Phi}^{\Pi}_{J}(\omega)}\,\bar{e}^{Q}_{if}(J0\Pi)\bar{e}(\vec{p}_0)\right), \tag{A1}$$

where $\omega^{(0)}_{if}$ stands for the mean frequency of the Q-branch transitions and $\hat{h}_0$ denotes the Liouville space operator radiating atom kinetic energy. The Liouville space vectors $\bar{e}^{Q}_{if}(J0\Pi)$ and $\bar{e}(\vec{p}_0)$ are given by

$$\bar{e}^{Q}_{if}(J0\Pi) = \sum_{jm}(-1)^{j-m}(2J+1)\varrho^{\frac{1}{2}}(E_j)\begin{pmatrix} j & J & j \\ -m & 0 & m\end{pmatrix}|v_f jm\rangle\,\langle v_i jm|, \tag{A2}$$

and

$$\bar{e}(\vec{p}_0) = \int d_3\vec{p}_0\varrho^{\frac{1}{2}}(\vec{p}_0)e_{\vec{p}_0\vec{\kappa}}. \tag{A3}$$

In the first approximation the line shape function is given in the line centre, by

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Im}\left(\bar{e}(\vec{p}_0), \frac{1}{\omega^{(0)}_{fi}-\omega+\hat{h}_0+\bar{\Phi}^{\Pi}_{J}(\omega^{(0)}_{if})}\,\bar{e}(\vec{p}_0)\right), \tag{A4}$$

where the averaged over all transition relaxation operator $\bar{\Phi}^{\Pi}_{J}$ is given by

$$\bar{\Phi}^{\Pi}_{J}(\omega^{(0)}_{fi}) = (\bar{e}^{Q}_{if}(J0\Pi), \hat{\Phi}(\omega^{(0)}_{fi})\bar{e}^{Q}_{if}(J0\Pi)). \tag{A5}$$

From the definition (A2) and the formula (26) of the text we get now

$$\begin{aligned}(e_{\vec{p}_0\vec{\kappa}}, \bar{\Phi}^{\Pi}_{J}(\omega^{(0)}_{fi})e_{\vec{p}_0\vec{\kappa}}) &= in(2\pi)^3\sum_{jb}\varrho(E_j)\varrho(b)\\ &\times\int d_3\vec{p}_1\varrho(\vec{p}_1)\Bigg(\mathrm{Im}\,\langle bv_i jm\vec{p}|T|b'v_i jm\vec{p}\rangle\delta(\vec{p}_0-\vec{p}_0')+2\pi(2J+1)\\ &\times\sum_{j'mm'b'}(-1)^{j+j'-m-m'}\begin{pmatrix} j & J & j \\ -m & 0 & m\end{pmatrix}\begin{pmatrix} j' & J & j' \\ -m' & 0 & m'\end{pmatrix}\langle bv_f jm\vec{p}|T|b'v_f j'm'\vec{p}'\rangle^*\\ &\times\delta(\varepsilon-\varepsilon')\,\langle bv_i jm\vec{p}|T|b'v_i j'm'\vec{p}'\rangle\Bigg).\end{aligned} \tag{A6}$$

In this formula the indices b stand for the quantum numbers of the internal motion of the perturbing molecules. Using the optical theorem we arrive at the following formula

$$
\begin{aligned}
(\bar{e}(\vec{p}_0), \Phi^{Q}(\omega_{fi}^{(0)})\bar{e}(\vec{p}_0)) &= in(2\pi)^4 \sum_{jj'bb'} \varrho(E_j)\varrho(b) \int d_3\vec{p}_0 \varrho(\vec{p}_0) \\
&\times \int d_3\vec{p}_1 \varrho(\vec{p}_1) \int d_3\vec{p}\,'_0 \Big(\langle bv_i jm\vec{p}|T|b'v_i j'm\vec{p}\,'\rangle \delta(\varepsilon-\varepsilon') \\
&\times \langle bv_i jm\vec{p}|T|b'v_i j'm\vec{p}\,'\rangle + (2J+1) \sum_{mm'} (-1)^{j+j'-m-m'} \begin{pmatrix} j & J & j \\ -m & 0 & m \end{pmatrix} \\
&\times \begin{pmatrix} j' & J & j' \\ -m' & 0 & m' \end{pmatrix} \langle bv_f jm\vec{p}|T|b'v_f j'm'\vec{p}\,'\rangle^* \delta(\varepsilon-\varepsilon') \langle bv_i jm\vec{p}|T|b'v_i j'm'\vec{p}\,'\rangle \Big), \qquad \text{(A7)}
\end{aligned}
$$

which appears in the text, in a bit simplified notation, as the formula (31).

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